Using a Temporary Silicon Connection in a Highly Stereoselective Synthesis of a New Class of Cyclic Allenylsilanes

Rui Ramalho,[a] Julien Beignet,[a,1] Alexander C. Humphries,[b] Liam R. Cox*[a]

[a] School of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK
Fax +44(121)4144403; E-mail: l.r.cox@bham.ac.uk

[b] The Neuroscience Research Centre, Merck, Sharp & Dohme, Terlings Park, Harlow, Essex, CM20 2QR, UK

Received 9 September 2005

Dedicated to Professor Steven Ley on the occasion of his 60th birthday, with particular thanks from two members of the group, ACH (1995–1998) and LRC (1994–1997)

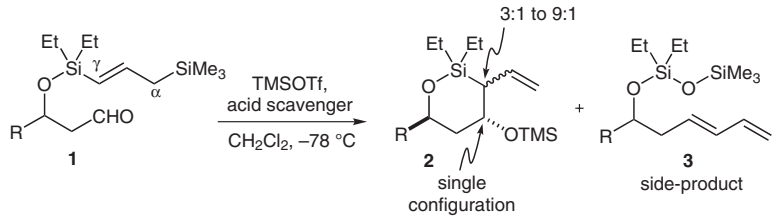
Abstract: Aldehyde **4** reacts in the presence of TMSOTf and an acid scavenger to provide the corresponding oxasilacycle **5** in very good yield and as a single diastereoisomer. The sense of 1,3-stereoinduction serves to introduce a 1,3-*syn*-diol relationship into the cyclic product. This is in accord with a previous study involving an analogous intramolecular allylation.

Key words: cyclisations, intramolecular allenylation, Lewis acids, stereoselective synthesis, Temporary Silicon Connection

Forming a tether between two reacting partners allows a subsequent reaction to proceed in an *intra*molecular fashion and benefit from the advantages associated with unimolecular processes. However, if the tether is then cleaved, the product obtained is the result of a net *inter*molecular reaction.[2] We recently employed such a strategy in the stereoselective allylation of a series of aldehydes **1**, in which the carbinol centre provided the site for appending an allylsilane through its γ-terminus (Scheme 1).[3] Aldehyde **1** reacted in the presence of TMSOTf and an acid scavenger,[4] providing the corresponding intramolecular allylation product, oxasilacycle **2**, in good yield. While levels of 1,4-stereoinduction were modest and rather substrate-dependent, 1,3-induction was consistently excellent; thus of the four possible diastereoisomeric products, only two were ever observed. We postulate that the adoption of reactive conformations in which the dipoles across the polar C–O and C=O bonds are opposed, are responsible for the high levels of 1,3-induction,[5] and that more subtle steric effects likely govern the 1,4-induction.[6]

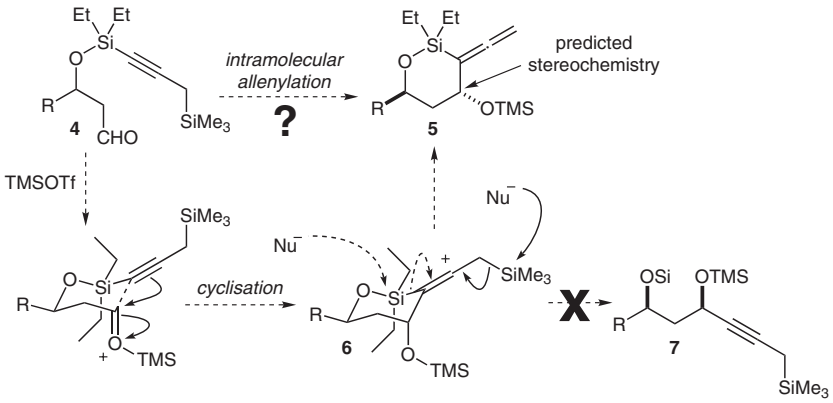
Acyclic dienes, **3**, were also obtained as side-products in these allylations. We believe that these products arise through a cascade process initiated by premature cleavage of the silyl ether tether in the collapse of the initially formed carbocationic intermediate.[7] This transformation provides an acyclic allylsilane which then undergoes a vinylogous silicon-mediated olefination[8] to provide the observed diene product.[9]

Replacing the allylsilane nucleophile in our cyclisation precursor with a propargylsilane would provide aldehyde **4**. In analogy with the reaction of aldehyde **1**, exposure of **4** to a Lewis acid should effect an intramolecular allenylation to provide a novel oxasilacycle, **5**, containing one new stereogenic centre and an allenylsilane moiety, which is ripe for further elaboration (Scheme 2).[10] We reasoned that such a reaction should be highly selective for a single stereoisomer since the formation of the allene moiety in **5** removes the issue of 1,4-stereoinduction, which had proven to be only modest in our previous allylation study (see Scheme 1).[3] This leaves just the issue of 1,3-induction to be considered. Since the factors governing the formation of this new carbinol stereocentre should be the same as those in our allylation study, a similar level and sense of 1,3-induction ought to be observed. Furthermore, since the silyl tether should be less efficient in stabilising the positive charge in the oxasilacyclic intermediate **6**,[11] the likelihood of premature tether collapse, resulting in the



Scheme 1 Reaction of an allylsilane tethered through a silyl ether to a β-hydroxy aldehyde provides a stereoselective route to a novel series of oxasilacycles.

SYNTHESIS 2005, No. 19, pp 3389–3397
Advanced online publication: 14.11.2005
DOI: 10.1055/s-2005-918465; Art ID: C06605SS



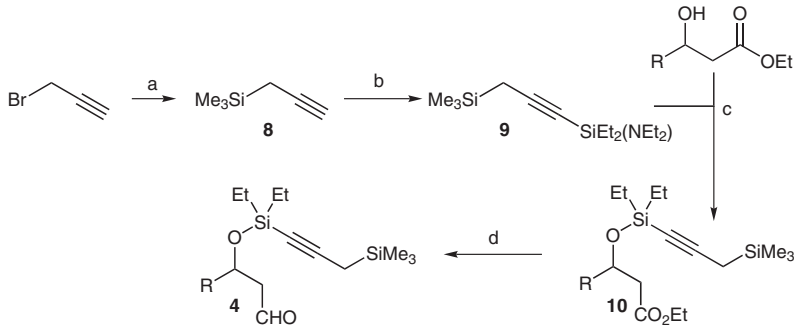
Scheme 2 A tethered propargylsilane should cyclise to provide a stereodefined allenylsilane product with high selectivity.

formation of an acyclic propargylsilane product **7**, should also be reduced (Scheme 2). Propargylsilanes have received far less attention than their allylsilane congeners.[12,13] We now report an extension of their synthetic utility to the synthesis of the chiral, cyclic allenylsilanes **5**.

We first required a synthesis of a γ-silyl-substituted propargylsilane possessing suitable functionality at the γ-terminus to allow the formation of the Temporary Silicon Connection in our cyclisation precursor. Encouraged by our previous success using aminosilanes as silyl etherification reagents in our allylsilane work,[3,7] we chose to investigate a similar strategy with this new class of nucleophile. Our first target was therefore γ-aminosilyl-substituted propargylsilane **9**, which was readily prepared in two steps (Scheme 3): reaction of propargyl magnesium bromide, readily prepared from propargyl bromide and Mg in the presence of $HgCl_2$, with TMSCl, provided propargyltrimethylsilane **8** along with a small amount (~5%) of allenyltrimethylsilane;[14,15] subsequent generation of the lithium acetylide of **8** with *n*-BuLi and trapping in situ with diethyl(diethylamino)chlorosilane[7,16] afforded **9** in very good yield. As expected, reaction of this silylating agent with a range of β-hydroxy esters[17] proceeded uneventfully to provide the corresponding silyl ethers **10**, and thence the aldehyde cyclisation precursors **4** after reduction of the ester functionality in **10** with DIBAL-H (Scheme 3).

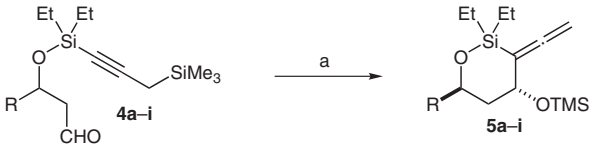
We were then ready to investigate the intramolecular allenylation. Previous work employing allylsilanes had revealed the extreme sensitivity of this type of reaction to the Lewis acid employed.[3] TMSOTf had provided the best results when used in conjunction with an acid scavenger[4] to remove adventitious triflic acid. Thus we were delighted to find that treating a solution of aldehyde **4** in CH_2Cl_2 at –78 °C, with an equimolar quantity of TMSOTf and a slight excess (1.2 equiv) of either 2,6-di-*tert*-butyl-4-methylpyridine (2,6-DTBMP) or tri-*tert*-butylpyrimidine (TTBP)[18] [both were equally effective acid scavengers although the latter was preferred (see below)], provided the desired cyclisation product **5** in good to very good isolated yield (Table 1). The reaction also proved to be highly stereoselective: analysis of the crude reaction mixture by NMR spectroscopy revealed the presence of only one diastereoisomer in every case. We therefore conservatively estimate the diastereoselectivity of this allenylation to be >95%. Products resulting from premature cleavage of the Temporary Silicon Connection were also not observed, even with aldehyde **4i**, which had been particularly prone to following this reaction pathway in the analogous intramolecular allylation.[3]

Since we had employed TMSOTf as the Lewis acid in the presence of an acid scavenger, products in which the generated alcohol is protected as its TMS ether were obtained. The high level of substitution around the ring clearly pro-



Scheme 3 *Reagents and conditions*: a) Mg, $HgCl_2$ (2 mol%), Et_2O, r.t., 1 h then Me_3SiCl, 0 °C to r.t., 2 h (48%); b) *n*-BuLi, THF, –78 °C to –50 °C, 1 h, then $Et_2Si(NEt_2)Cl$, –78 °C to r.t., 1 d (88%); c) imidazole, DMAP, CH_2Cl_2, r.t., 18 h (57–91%); d) DIBAL-H, –78 °C, CH_2Cl_2, 1 h (40–95%).

Table 1 TMSOTf-Mediated Allenylation of Aldehyde **4** Provided a Single Diastereoisomeric Oxasilacyclic Product **5**[a]



Aldehyde **4**	R	Yield of **5** (%)[b]
a	Ph	80
b	2-furyl	72
c	(*E*)-cinnamyl	73
d	TIPS-C≡C	85
e	cyclohexyl	68
f	*s*-Bu	83
g	*n*-Bu	66
h	$BnOCH_2CH_2$	70
i	Me	67

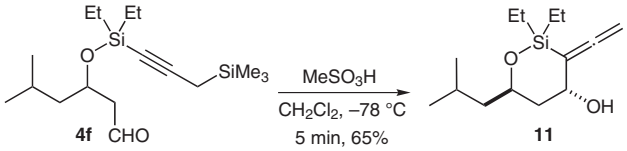
[a] *Reagents and conditions*: TMSOTf, 2,6-DTBMP or TTBP, CH_2Cl_2, –78 °C, 18 h.
[b] Isolated yield of **5** following purification by column chromatography.

tects this potentially labile silyl protecting group, which survived a standard aqueous work-up and product purification by flash column chromatography on silica gel. However, the very low polarity of the oxasilacycles called for care in separating the desired product from the non-polar acid scavengers, especially 2,6-DTBMP (relative polarity: TTBP > 2,6-DTBMP ~ **5**). Since all attempts to deprotect the TMS ether selectively led to product decomposition, we investigated a number of modifications to our method that might improve matters:

1) A polymer-supported acid scavenger would allow its facile separation from the allene product by filtration, as well as permit its potential reuse after regeneration of the free base.[19] Polymer-supported 2,6-DTBMP[20] is commercially available, albeit expensive. However in our hands, its use led to inferior results compared with its organic-soluble analogue.

2) Theoretically, it should be possible to employ the Lewis acid in sub-stoichiometric quantities as the 'TMS$^+$' activator should be regenerated after each cyclisation. This in turn would allow the use of reduced quantities of the acid scavenger, and again facilitate the purification step. However when aldehyde **4a** was treated with 20 mol% TMSOTf in the presence of 50 mol% 2,6-DTBMP, the reaction failed to go to completion; indeed complete conversion could only be achieved with stoichiometric quantities of Lewis acid.

3) The reason for using an acid scavenger in the first place had been to remove adventitious triflic acid from the reaction mixture, as our work with the corresponding allylsilanes had shown that Brønsted acids rapidly cleaved the silyl ether tether or led exclusively to diene products.[21] Since elimination pathways were not a problem in the present study, we replaced the Lewis acid activator with a Brønsted acid and did away with the base altogether. Reaction of aldehyde **4f** with methanesulfonic acid resulted in the rapid (5 min) consumption of starting material at –78 °C and concomitant formation of the oxasilacycle **11** in an encouraging 65% yield (Scheme 4).

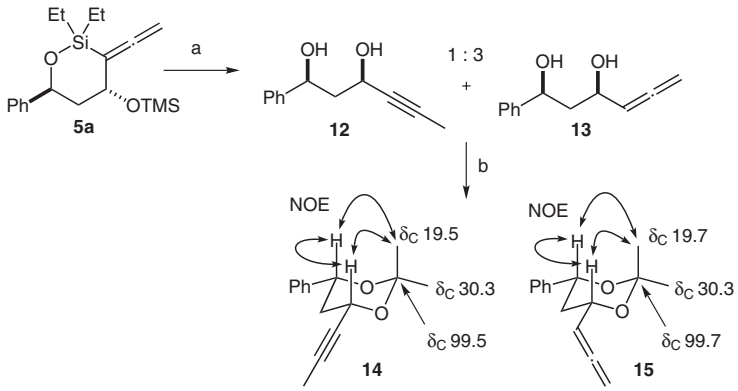


Scheme 4 Brønsted acid mediated cyclisation provides an alcohol product.

We provisionally assigned the sense of 1,3-induction in **5** by analogy with that observed in our allylation study.[3] However, we were keen to confirm the result independently. Since NMR studies, including NOE experiments, on the cyclisation products proved inconclusive, we chose to remove the tether and investigate the ring-opened protodesilylated product. Reaction of **5a** with KF in a MeOH–THF solvent mix at 60 °C effected clean protodesilylation[22] and the formation of two diol products **12** and **13**, with the allene **13** resulting from *ipso* protodesilylation accounting for the major product (Scheme 5). Exposure of this diol mixture to acetone in the presence of PTSA and Na_2SO_4 provided the corresponding acetonides **14** and **15**. In accordance with Rychnovsky's observations,[23] analysis of the ^{13}C NMR spectra of **14** and **15** allowed the assignment of a 1,3-*syn* diol relationship in both products, thus confirming the stereochemical outcome that we had predicted based on our previous results. Further corroboration was achieved by NOE experiments (Scheme 5).

In summary, we have shown that forming a 'Temporary Silicon Connection' between a propargylsilane and a β-hydroxyaldehyde allows a highly stereoselective intramolecular allenylation to take place in the presence of TMSOTf and an acid scavenger. The reaction is general for a wide range of aldehydes and provides a single stereoisomeric product in good to excellent yield. Preliminary results suggest that Brønsted acids might also be able to effect this cyclisation. Optimisation of this process, together with the development of novel ways in which to elaborate the allene products, are the focus of ongoing and future studies.

Elemental analyses were recorded on a Carlo Erba EA1110 simultaneous CHNS analyser. IR spectra were recorded neat as thin films on a Perkin-Elmer FT-IR PARAGON 1000 or a Spectrum 1000 spectrometer. ^1H NMR spectra were recorded at ambient temperature unless stated otherwise on a Bruker AC-300 (300 MHz), AMX 400 (400 MHz), DRX-500 (500 MHz) or DPX-500 (500 MHz) spectrometer. The term 'stack' is used to describe a region where



Scheme 5 *Reagents and conditions*: a) KF, $KHCO_3$, THF–MeOH, 70 °C, 1.5 h, 76%; b) acetone, PTSA, Na_2SO_4, quant.

resonances arising from non-equivalent nuclei are coincident. 'Multiplet', m, is used to describe a region where a resonance arises from a single nucleus (or equivalent nuclei) but where coupling constants cannot be assigned. Residual protic solvent $CHCl_3$ (δ_H = 7.26) was used as an internal reference. ^{13}C NMR spectra were recorded at ambient temperature unless stated otherwise on a Bruker AC-300 (75 MHz), AV-300 (75 MHz), DPX-360 (90 MHz), AMX-400 (100 MHz) or DRX-500 (125 MHz) spectrometer. The central resonance of $CDCl_3$ (δ_C = 77.0) was used as an internal reference. Unit mass resolution mass spectra were recorded on a Micromass LCT spectrometer (TOF-ES+), or a Micromass ZMD spectrometer. HRMS were recorded on a Micromass LCT spectrometer or a Micromass Micro QToF spectrometer, using a lock mass incorporated into the mobile phase. All reagents were obtained from commercial sources and used without further purification unless stated otherwise. Propargyltrimethylsilane was prepared according to a literature procedure[14] and purified by reduced pressure distillation (106 mbar). The distillate comprised a 55:37:5:3 mixture of propargyltrimethylsilane:toluene:Et_2O:allenyltrimethylsilane (as determined by ^1H NMR) which was used without further purification (note: propargyl bromide was purchased as a solution in toluene). THF and Et_2O were distilled from sodium benzophenone ketyl. All solutions are aqueous and saturated, unless otherwise stated. All reactions were conducted in flame-dried glassware under N_2, and at ambient temperature (19 to 25 °C) unless otherwise stated, with magnetic stirring. Volumes of 1 mL or less were measured and dispensed with Hamilton gastight syringes. Flash column chromatography was carried out using Fluka 60 (40–60 μm mesh) or BDH (33–70 μm mesh) silica gel. Analytical TLC was performed on Whatman or Fluka 60 Å 0.25 mm pre-coated glass-backed plates and visualised by UV (254 nm), $KMnO_4$ solution and $(NH_4)_2MoO_4/Ce(SO_4)_2$ solution. Evaporation and concentration under reduced pressure were performed at 50–500 mbar. Residual solvent was removed under high vacuum (1 mbar).

3-[Diethyl(diethylamino)silyl]propargyltrimethylsilane (9)

n-BuLi (24 mL, 58 mmol, 2.4 M in hexane) was added dropwise over 30 min to a solution of propargyltrimethylsilane (53 mmol, prepared as a solution in Et_2O and toluene) in THF (106 mL) at –78 °C. The mixture was stirred at this temperature for 1 h and then at –50 °C for 30 min, before re-cooling to –78 °C. Diethyl(diethylamino)chlorosilane (10.2 mL, 53 mmol) was then added dropwise over 15 min. The mixture was allowed to warm to r.t. over 12 h and then stirred for a further 12 h. The solution was transferred to a dry flask and separated from the precipitated LiCl salts using a cannula fitted with an oven-dry Whatman filter paper 1. Concentration of the solution under reduced pressure (400 mbar) afforded a red-orange liquid, which was rapidly transferred to a 50-mL round-bottomed flask. Purification by reduced pressure distillation afforded propargyl silane **9** as a colourless liquid (12.5 g, 88%); bp 128 °C/49 mbar. The moisture sensitivity of this compound precluded full characterisation.

IR (film): 2958s, 2874s, 2154s (C≡C), 1461m, 1413m, 1374s, 1342m, 1292m, 1250s, 1233m, 1204s, 1174s, 1148m, 1029s, 1007s, 923m, 852s, 761s, 726s cm^{-1}.

^1H NMR (300 MHz, C_6D_6): δ = 0.09 [s, 9 H, $Si(CH_3)_3$], 0.76 [q, *J* = 7.7, 4 H, $Si(CH_2CH_3)_2$], 1.09 [t, *J* = 7.0, 6 H, $N(CH_2CH_3)_2$], 1.20 [t, *J* = 7.7, 6 H, $Si(CH_2CH_3)_2$], 1.46 (s, 2 H, $C{\equiv}CCH_2$), 2.96 [q, *J* = 7.0, 4 H, $N(CH_2CH_3)_2$].

^{13}C NMR (75 MHz, C_6D_6): δ = –2.2 [$Si(CH_3)_3$], 7.4 [$Si(CH_2CH_3)_2$], 7.7 [$Si(CH_2CH_3)_2$], 8.8 ($C{\equiv}CCH_2$), 15.9 [$N(CH_2CH_3)_2$], 40.4 [$N(CH_2CH_3)_2$], 81.0 (*C*≡C), 105.4 (C≡*C*).

Silyletherification of β-Hydroxy Esters to Silyl Ethers 10; General Procedure

A solution of the β-hydroxy ester (2.5 mmol) in CH_2Cl_2 (25 mL) was added to a flask charged with aminosilane **9** (2.5 mmol), imidazole (5.1 mmol) and DMAP (5 mol%). The reaction was stirred overnight at r.t., and after approximately 18 h, quenched by the addition of $NaHCO_3$ solution (20 mL). The mixture was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic extracts were washed with brine (20 mL) and dried ($MgSO_4$). Removal of the solvent under reduced pressure and purification by flash column chromatography (eluent: hexane–Et_2O) afforded silyl ether **10** as a colourless oil (Table 2).

Reduction of Esters 10 to Aldehydes 4; General Procedure

DIBAL-H (1.5 mmoL, 1.5 M in toluene) was added dropwise over 5 min to a solution of ester **10** (1.2 mmol) in CH_2Cl_2 (12 mL) at –78 °C. The progress of the reaction was monitored by TLC. Upon consumption of starting material (generally 1 h), the reaction was quenched by the dropwise addition of MeOH (1.2 mmol) and then dropwise addition of H_2O (6.0 mmol). The resulting slurry was warmed to r.t. and then filtered through a pad of $MgSO_4$ and Celite, and washed with CH_2Cl_2 (4 × 25 mL). Concentration of the filtrate under reduced pressure and purification of the residue by flash column chromatography (eluent: hexane–Et_2O) afforded aldehyde **4** as a colourless oil (Table 3).

Table 2 Characterisation Data for Esters **10**

10[a,b]	^{1}H NMR ($CDCl_3$) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$) δ	TOF-MS *m/z* (%)	Yield (%)
a	0.09 [s, 9 H, $Si(CH_3)_3$], 0.42 (q, *J* = 7.7, 2 H, $SiCH_2CH_3$), 0.58 (q, *J* = 7.7, 2 H, $SiCH_2CH_3$), 0.80 (t, *J* = 7.7, 3 H, $SiCH_2CH_3$), 0.95 (t, *J* = 7.7, 3 H, $SiCH_2CH_3$), 1.21 (t, *J* = 7.5, 3 H, OCH_2CH_3), 1.54 (s, 2 H, CH_2TMS), 2.61 (dd, *J* = 14.6, 5.3, 1 H, CH_aH_bCO), 2.80 (dd, *J* = 14.6, 8.4, 1 H, CH_aH_bCO), 4.02–4.28 (m, 2 H, OCH_2CH_3), 5.32 (dd, *J* = 8.4, 5.3, 1 H, CHOSi), 7.19–7.40 (stack, 5 H, C_6H_5)	–2.1, 6.6 (2 ×), 6.8, 7.1, 8.7, 14.1, 45.8, 60.3, 72.4, 78.8, 107.4, 126.0, 127.4, 128.1, 143.6, 170.8	413.1 (100)	91
b	0.11 [s, 9 H, $Si(CH_3)_3$], 0.42–0.72 [stack, 4 H, $Si(CH_2CH_3)_2$], 0.83 (t, *J* = 7.9, 3 H, CH_2CH_3), 0.95 (t, *J* = 8.0, 3 H, CH_2CH_3), 1.22 (t, *J* = 7.3, 3 H, OCH_2CH_3), 1.58 (s, 2 H, CH_2TMS), 2.79 (dd, *J* = 15.1, 6.2, 1 H, CH_aH_bCO), 2.91 (dd, *J* = 15.1, 7.8, 1 H, CH_aH_bCO), 4.02–4.18 (m, 2 H, OCH_2CH_3), 5.36 (dd, *J* = 7.8, 6.2, 1 H, CHOSi), 6.24 (d, *J* = 2.9, 1 H_{furyl}), 6.28 (dd, *J* = 2.9, 1.8, 1 H_{furyl}), 7.31–7.35 (m, 1 H_{furyl})	–2.2, 6.3, 6.5, 6.6, 7.0, 8.7, 14.1, 41.8, 60.3, 65.7, 78.4, 106.4, 107.6, 110.0, 141.7, 155.7, 170.3	403.1 (100)	86
c	0.10 [s, 9 H, $Si(CH_3)_3$], 0.58–0.69 [stack, 4 H, $Si(CH_2CH_3)_2$], 0.98 [t, *J* = 7.7, 6 H, $Si(CH_2CH_3)_2$], 1.24 (t, *J* = 7.0, 3 H, OCH_2CH_3), 1.56 (s, 2 H, CH_2TMS), 2.50 (dd, *J* = 14.4, 6.4, 1 H, CH_aH_bCO), 2.71 (dd, *J* = 14.4, 7.4, 1 H, CH_aH_bCO), 4.07–4.19 (m, 2 H, OCH_2CH_3), 4.93 (app q, *J* = 6.3, 1 H, CHOSi), 6.23 (dd, *J* = 15.9, 6.6, 1 H, =CHCHO), 6.60 (d, *J* = 15.9, 1 H, PhCH=), 7.19–7.39 (stack, 5 H, C_6H_5)	–2.2, 6.60, 6.64, 6.8, 7.3, 8.7, 14.2, 43.6, 60.3, 71.0, 79.0, 107.4, 126.5, 127.4, 128.4, 130.1, 131.1, 136.8, 170.7	439.3 (100)	70
d	0.01 [s, 9 H, $Si(CH_3)_3$], 0.56–0.74 [stack, 4 H, $Si(CH_2CH_3)_2$], 0.93–0.99 [stack, 6 H, $Si(CH_2CH_3)_2$], 1.04 {s, 21 H, $Si[CH(CH_3)_2]_3$}, 1.25 (t, *J* = 7.4, 3 H, OCH_2CH_3), 1.55 (s, 2 H, CH_2TMS), 2.68 (dd, *J* = 14.9, 6.2, 1 H, CH_aH_bCO), 2.78 (dd, *J* = 14.9, 7.7, 1 H, CH_aH_bCO), 4.08–4.17 (m, 2 H, OCH_2CH_3), 5.03 (dd, *J* = 7.7, 6.2, 1 H, CHOSi)	–2.1, 6.5, 6.6, 6.8, 7.2, 8.7, 11.1, 14.1, 18.4, 44.2, 60.4, 60.7, 78.2, 85.1, 107.5, 107.9, 169.8	517.3 (100), 383.3 (10)	57
e	0.12 [s, 9 H, $Si(CH_3)_3$], 0.55–0.66 [stack, 4 H, $Si(CH_2CH_3)_2$], 0.88–1.30 [stack, 14 H, $Si(CH_2CH_3)_2$, 5 × Cy*H*, OCH_2CH_3], 1.42–1.80 (stack, 8 H, 6 × Cy*H*, CH_2TMS), 2.39–2.54 (stack, 2 H, CH_2CO_2Et), 3.97–4.15 (stack, 3 H, CHOSi, OCH_2CH_3)	–2.1, 6.7, 6.8, 7.0, 7.2, 8.8, 14.2, 26.3, 26.4, 26.6, 28.1, 28.5, 39.6, 43.6, 60.2, 74.2, 79.5, 106.9, 172.3	439.3 (100)	67
f	0.11 [s, 9 H, $Si(CH_3)_3$], 0.62 [q, *J* = 7.7, 4 H, $Si(CH_2CH_3)_2$], 0.90 [d, *J* = 6.6, 3 H, 1 × $CH(CH_3)_2$], 0.92 [d, *J* = 6.2, 3 H, 1 × $CH(CH_3)_2$], 0.97 [t, *J* = 7.7, 6 H, $Si(CH_2CH_3)_2$], 1.25 (t, *J* = 7.2, 3 H, OCH_2CH_3), 1.44–1.60 (stack, 4 H, CH_2TMS, *i*-PrCH_2), 1.65–1.79 [m, 1 H, $CH(CH_3)_2$], 2.42 (dd, *J* = 14.7, 6.6, 1 H, CH_aH_bCO), 2.57 (dd, *J* = 14.7, 6.3, 1 H, CH_aH_bCO), 4.06–4.19 (m, 2 H, CH_2CH_3), 4.28–4.38 (m, 1 H, CHOSi)	–2.1, 6.7 (2 ×), 7.12, 7.14, 8.8, 14.2, 22.3, 23.3, 24.4, 43.1, 46.6, 60.1, 68.6, 79.3, 107.2, 171.5	393.1 (100)	89
g	0.11 [s, 9 H, $Si(CH_3)_3$], 0.59 [q, *J* = 7.7, 4 H, $Si(CH_2CH_3)_2$], 0.82–1.01 [stack, 9 H, $Si(CH_2CH_3)_2$, CH_3], 1.18–1.38 (stack, 7 H, OCH_2CH_3, 2 × CH_2), 1.47–1.60 (stack, 4 H, CH_2TMS, CH_2), 2.42 (dd, *J* = 14.7, 6.3, 1 H, CH_aH_bCO), 2.57 (dd, *J* = 14.7, 7.0, 1 H, CH_aH_bCO), 4.11 (q, *J* = 7.0, 2 H, OCH_2CH_3), 4.25 (app quintet, *J* = 6.2, 1 H, CHOSi)	–1.2, 6.6 (2 ×), 6.9, 7.1, 8.6, 14.1, 14.2, 22.6, 27.3, 36.8, 42.5, 60.4, 70.1, 79.2, 107.0, 171.5	393.2 (100)	91
h	0.08 [s, 9 H, $Si(CH_3)_3$], 0.52–0.62 [stack, 4 H, $Si(CH_2CH_3)_2$], 0.91–0.96 [stack, 6 H, $Si(CH_2CH_3)_2$], 1.25 (t, *J* = 7.0, 3 H, OCH_2CH_3), 1.53 (s, 2 H, CH_2TMS), 1.81–1.89 (stack, 2 H, $BnOCH_2CH_2$), 2.48 (dd, *J* = 14.7, 6.2, 1 H, CH_aH_bCO), 2.58 (dd, *J* = 14.7, 6.6, 1 H, CH_aH_bCO), 3.56 (t, *J* = 6.6, 2 H, $BnOCH_2$), 4.05–4.12 (stack, 2 H, OCH_2CH_3), 4.37–4.51 (stack, 3 H, CHOSi, $PhCH_2$), 7.23–7.31 (stack, 5 H, C_6H_5)	–2.2, 6.53, 6.56, 6.8, 6.9, 8.6, 14.1, 36.9, 42.6, 60.0, 66.7, 67.6, 72.7, 79.1, 107.1, 127.2, 127.4, 128.1, 138.5, 171.1	471.1 (100)	66
i	0.11 [s, 9 H, $Si(CH_3)_3$], 0.59 [q, *J* = 7.5, 4 H, $Si(CH_2CH_3)_2$], 0.96 [t, *J* = 7.5, 6 H, $Si(CH_2CH_3)_2$], 1.23–1.28 (stack, 6 H, CH_3, OCH_2CH_3), 1.58 (s, 2 H, CH_2TMS), 2.38 (dd, *J* = 14.4, 6.3, 1 H, CH_aH_bCO), 2.58 (dd, *J* = 14.4, 7.0, 1 H, CH_aH_bCO), 4.06–4.15 (m, 2 H, OCH_2CH_3), 4.36–4.47 (m, 1 H, CHOSi)	–2.7, 6.1 (2 ×), 6.4, 6.7, 8.2, 13.7, 23.1, 44.3, 59.9, 66.3, 79.1, 107.1, 171.8	351.2 (100)	78

[a] Satisfactory microanalyses obtained for **10a**–**g**: C ± 0.42, H ± 0.41.
10h: HRMS: *m/z* [(M + Na)$^+$] calcd for $C_{24}H_{40}O_4Si_2$ + Na: 471.2363; found: 471.2367.
10i: HRMS: *m/z* [(M + Na)$^+$] calcd for $C_{16}H_{32}O_3Si_2$ + Na: 351.1788; found: 351.1784.
[b] All compounds showed the characteristic peaks for acetylenic and carbonyl bonds. IR (film): 2154s (C≡C), 1740s cm^{-1} (C=O).

Table 3 Characterisation Data for Aldehydes **4**

4[a]	^{1}H NMR ($CDCl_3$, 300 MHz) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$, 75 MHz), δ	TOF-MS *m*/*z* (%)	HRMS	Yield (%)
a	0.10 [s, 9 H, Si(CH_3)$_3$], 0.42 (q, *J* = 8.1, 2 H, CH_2CH$_3$), 0.57–0.66 (m, 2 H, CH_2CH$_3$), 0.78 (t, *J* = 8.1, 3 H, CH$_2$CH_3), 0.97 (t, *J* = 7.7, 3 H, CH$_2$CH_3), 1.56 (s, 2 H, CH_2TMS), 2.68 (ddd, *J* = 15.8, 4.4, 2.2, 1 H, CH_aH$_b$), 2.83 (ddd, *J* = 15.8, 8.1, 2.9, 1 H, CH$_a$$H_b$), 5.42 (dd, *J* = 8.1, 4.4, 1 H, CHOSi), 7.25–7.34 (stack, 5 H, C$_6$H$_5$), 9.81 (app t, *J* = 2.5, 1 H, CHO)	–2.1, 6.3, 6.4, 6.7, 7.1, 8.7, 53.4, 71.0, 78.5, 108.1, 125.7, 127.5, 128.3, 143.3, 201.6	401.2 [100, (M + Na + MeOH)$^+$], 369.2 (15, M$^+$)	*m*/*z* [(M + Na + MeOH)$^+$] calcd for C$_{19}$H$_{30}$O$_2$Si$_2$ + Na + MeOH: 401.1944; found: 401.1953	95
b	0.12 [s, 9 H, Si(CH_3)$_3$], 0.47–0.67 [stack, 4 H, Si(CH_2CH$_3$)$_2$], 0.86 (t, *J* = 7.9, 3 H, CH$_2$CH_3), 0.97 (t, *J* = 7.9, 3 H, CH$_2$CH_3), 1.60 (s, 2 H, CH_2TMS), 2.82 (ddd, *J* = 16.2, 5.3, 2.4, 1 H, CH_aH$_b$), 2.96 (ddd, *J* = 16.2, 7.3, 2.6, 1 H, CH$_a$$H_b$), 5.43 (dd, *J* = 7.3, 5.3, 1 H, CHOSi), 6.24–6.26 (m, 1 H$_{furyl}$), 6.30–6.32 (m, 1 H$_{furyl}$), 7.35–7.36 (m, 1 H$_{furyl}$), 9.83 (app t, *J* = 2.4, 1 H, CHO)	–2.2, 6.3, 6.4, 6.6, 7.0, 8.7, 49.5, 64.4, 78.3, 106.7, 108.3, 110.1, 141.9, 154.9, 200.8	359.0 (100)	*m*/*z* [(M + Na)$^+$] calcd for C$_{17}$H$_{28}$O$_3$Si$_2$ + Na: 359.1475; found: 359.1481	40
c	0.10 [s, 9 H, Si(CH_3)$_3$], 0.59–0.71 [stack, 4 H, Si(CH_2CH$_3$)$_2$], 0.93–1.02 [stack, 6 H, Si(CH$_2$CH_3)$_2$], 1.58 (s, 2 H, CH_2TMS), 2.60–2.77 (stack, 2 H, CH_2CHO), 5.03 (app q, *J* = 6.1, 1 H, CHOSi), 6.24 (dd, *J* = 15.8, 6.2, 1 H, =CHCHOSi), 6.62 (d, *J* = 15.8, 1 H, PhCH=), 7.21–7.38 (stack, 5 H, C$_6$H$_5$), 9.84 (app. t, *J* = 2.2, 1 H, CHO)	–2.1, 6.61, 6.64, 6.8, 7.3, 8.7, 51.3, 69.6, 78.7, 108.1, 126.5, 127.7, 128.5, 130.2, 131.0, 136.5, 201.6	427.3 [100, (M + Na + MeOH)$^+$], 395.3 (18)	*m*/*z* [(M + Na)$^+$] calcd for C$_{21}$H$_{32}$O$_2$Si$_2$ + Na: 395.1839; found: 395.1837	67
d	0.11 [s, 9 H, Si(CH_3)$_3$], 0.57–0.75 [stack, 4 H, Si(CH_2CH$_3$)$_2$], 0.83–0.99 {stack, 27 H, Si(CH$_2$CH_3)$_2$, Si[CH(CH_3)$_2$]$_3$}, 1.58 (s, 2 H, CH_2TMS), 2.63–2.80 (stack, 2 H, CH_2CHO), 5.07 (app t, *J* = 5.9, 1 H, CHOSi), 9.86 (app t, *J* = 2.2, 1 H, CHO)	–2.1, 6.5, 6.66, 6.74, 7.2, 8.8, 11.1, 18.5, 51.3, 59.2, 78.1, 86.6, 107.0, 108.4, 200.8	473.4 (100)	*m*/*z* [(M + Na)$^+$] calcd for C$_{24}$H$_{46}$O$_2$Si$_3$ + Na: 473.2703; found: 473.2704	90
e	0.11 [s, 9 H, Si(CH_3)$_3$], 0.56–0.66 [stack, 4 H, Si(CH_2CH$_3$)$_2$], 0.93–1.00 [stack, 8 H, Si(CH$_2$CH_3)$_2$ + 2 × CyH], 1.07-1.23 (stack, 3 H, 3 × CyH), 1.43–1.76 (stack, 8 H, 6 × CyH, CH_2TMS), 2.52–2.55 (stack, 2 H, CH_2CHO), 4.16 (app q, *J* = 5.8, 1 H, CHOSi), 9.83 (app t, *J* = 2.6, 1 H, CHO)	–2.2, 6.55, 6.59, 7.0, 7.1, 8.6, 26.1 (2 ×), 26.4, 28.1, 28.6, 43.8, 47.7, 72.9, 79.0, 107.6, 202.4	407.3 [85, (M + Na + MeOH)$^+$], 375.3 (100)	*m*/*z* [(M + Na)$^+$] calcd for C$_{19}$H$_{36}$O$_2$Si$_2$ + Na: 375.2152; found: 375.2166	56
f	0.11 [s, 9 H, Si(CH_3)$_3$], 0.57–0.66 [stack, 4 H, Si(CH_2CH$_3$)$_2$], 0.89–1.00 [stack, 12 H, Si(CH$_2$CH_3)$_2$, CH(CH_3)$_2$], 1.25–1.34 (m, 1 H, *i*-PrCH_aH$_b$), 1.54–1.58 (stack, 3 H, *i*-PrCH$_a$$H_b$, CH$_2$TMS), 1.65–1.73 [m, 1 H, CH(CH$_3$)$_2$], 2.48–2.62 (stack, 2 H, CH_2CHO), 4.39–4.50 (m, 1 H, CHOSi), 9.84 (app t, *J* = 2.2, 1 H, CHO)	–2.1, 6.6 (2 ×), 7.1, 7.2, 8.7, 22.5, 23.0, 24.4, 46.8, 51.1, 67.4, 79.0, 107.9, 202.4	381.0 [100, (M + Na + MeOH)$^+$], 349.0 (75)	*m*/*z* [(M + Na)$^+$] calcd for C$_{17}$H$_{34}$O$_2$Si$_2$ + Na: 349.1995; found: 349.2000	92
g	0.11 [s, 9 H, Si(CH_3)$_3$], 0.56–0.65 [stack, 4 H, Si(CH_2CH$_3$)$_2$], 0.86–0.91 (m, 3 H, CH$_3$), 0.91–1.00 [stack, 6 H, Si(CH$_2$CH_3)$_2$], 1.25–1.34 (stack, 4 H, 2 × CH$_2$), 1.54–1.60 (stack, 4 H, CH$_2$, CH_2TMS), 2.52–2.57 (stack, 2 H, CH_2CHO), 4.35 (app quintet, *J* = 6.1, 1 H, CHOSi), 9.84 (app t, *J* = 2.2, 1 H, CHO)	–2.2, 6.51, 6.53, 6.9, 7.1, 8.5, 13.9, 22.5, 27.3, 37.2, 50.6, 69.0, 78.9, 107.6, 202.1	381.3 [65, (M + Na + MeOH)$^+$], 349.3 (100)	*m*/*z* [(M + Na)$^+$] calcd for C$_{17}$H$_{34}$O$_2$Si$_2$ + Na: 349.1995; found: 349.1996	47
h	0.10 [s, 9 H, Si(CH$_3$)$_3$], 0.42 [q, *J* = 7.6, 4 H, Si(CH_2CH$_3$)$_2$], 0.96 [t, *J* = 7.7, 6 H, Si(CH$_2$CH_3)$_2$], 1.56 (s, 2 H, CH_2TMS), 1.81–1.95 (stack, 2 H, BnOCH$_2$CH_2), 2.52–2.70 (stack, 2 H, CH_2CHO), 3.56 (t, *J* = 6.0, 2 H, BnOCH_2), 4.43–4.59 (stack, 3 H, CHOSi + PhCH_2), 7.25–7.36 (stack, 5 H, C$_6$H$_5$), 9.81 (app t, *J* = 2.2, 1 H, CHO)	–2.1, 6.56, 6.60, 6.9, 7.0, 8.6, 37.3, 50.8, 66.42, 66.45, 72.9, 78.9, 107.9, 127.4, 127.5, 128.2, 138.3, 202.0	459.4 [100, (M + Na + MeOH)$^+$], 427.3 (90)	*m*/*z* [(M + Na)$^+$] calcd for C$_{22}$H$_{36}$O$_3$Si$_2$ + Na 427.2101; found: 427.2112	90
i	0.11 [s, 9 H, Si(CH_3)$_3$], 0.55–0.74 [stack, 4 H, Si(CH_2CH$_3$)$_2$], 0.96 (t, *J* = 8.1, 3 H, CH$_2$CH_3), 0.97 (t, *J* = 7.7, 3 H, CH$_2$CH_3), 1.26 (d, *J* = 6.2, 3 H, CH$_3$), 1.58 (s, 2 H, CH_2TMS), 2.43–2.61 (stack, 2 H, CH_2CHO), 4.46–4.54 (m, 1 H, CHOSi), 9.80 (app t, *J* = 2.2, 1 H, CHO)	–2.1, 6.6 (2 ×), 6.8, 7.3, 8.7, 23.8, 52.7, 65.2, 78.9, 107.6, 202.3	339.3 [45, (M + Na + MeOH)$^+$], 307.3 (100)	*m*/*z* [(M + Na)$^+$] calcd for C$_{14}$H$_{28}$O$_2$Si$_2$ + Na: 307.1526; found: 307.1535	94

[a] All compounds showed the characteristic peaks for acetylenic and carbonyl bonds. IR (film): 2152s (C≡C), 1728s cm^{-1} (C=O).

Intramolecular Allenylation of Aldehydes 4; General Procedure

TMSOTf (2.0 mmol) was added dropwise over 5 min to a solution of aldehyde **4** (2.0 mmol) and 2,6-DTBMP or TTBP (2.4 mmol) in CH_2Cl_2 (24 mL) at –78 °C. The mixture was stirred at –78 °C and monitored by TLC. After approximately 18 h, $NaHCO_3$ solution (15 mL) was added and the solution allowed to warm to r.t. The mixture was extracted with CH_2Cl_2 (2 × 30 mL) and the combined organic extracts were washed with brine (25 mL) and dried ($MgSO_4$). Removal of the solvent under reduced pressure and purification of the residue by flash column chromatography (eluent: hexane–Et_2O) afforded the allene **5** as a colourless oil (Table 4).

Table 4 Characterisation Data for Allenes **5**

5[a]	^{1}H NMR ($CDCl_3$, 300 MHz) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$, 75 MHz), δ	TOF-MS *m/z* (%)	HRMS	Yield (%)
a	0.13 [s, 9 H, $Si(CH_3)_3$], 0.71–0.86 [stack, 4 H, $Si(CH_2CH_3)_2$], 0.96–1.08 [stack, 6 H, $Si(CH_2CH_3)_2$], 1.73–1.82 (m, 1 H, CH_aH_b), 1.87–1.94 (m, 1 H, CH_aH_b), 4.37–4.39 (stack, 2 H, $=CH_2$), 4.64–4.65 (m, 1 H, CHOTMS), 5.35 (dd, *J* = 11.0, 1.8, 1 H, PhCHO), 7.21–7.36 (stack, 5 H, C_6H_5)	0.2, 5.4, 6.4, 6.5, 7.7, 46.5, 68.8, 69.9, 71.5, 91.6, 125.4, 126.9, 128.2, 145.3, 207.7	369.2 (100)	*m/z* [(M + Na)$^+$] calcd for $C_{19}H_{30}O_2Si_2$ + Na: 369.1682; found: 369.1689	80
b	0.11 [s, 9 H, $Si(CH_3)_3$], 0.64–0.75 (stack, 2 H, CH_2CH_3), 0.75–0.80 (stack, 2 H, CH_2CH_3), 0.95–1.04 [stack, 6 H, $Si(CH_2CH_3)_2$], 1.96–2.04 (stack, 2 H, CH_2), 4.42 (s, 2 H, $=CH_2$), 4.67–4.69 (m, 1 H, CHOTMS), 5.36 (dd, *J* = 9.2, 3.7, 1 H, $CHOSiEt_2$), 6.21 (d, *J* = 2.9, 1 H_{furyl}), 6.30–6.32 (m, 1 H_{furyl}), 7.34 (br s, 1 H_{furyl})	0.1, 5.5, 6.32, 6.45, 7.6, 41.8, 64.2, 69.1, 70.8, 91.8, 105.3, 110.0, 141.6, 157.3, 207.7	359 (100), 301 (13)	*m/z* [(M + Na)$^+$] calcd for $C_{17}H_{28}O_3Si_2$ + Na: 359.1475; found: 359.1484	72
c	0.12 [s, 9 H, $Si(CH_3)_3$], 0.66–0.89 [stack, 4 H, $Si(CH_2CH_3)_2$], 0.93–1.03 [stack, 6 H, $Si(CH_2CH_3)_2$], 1.64–1.73 (m, 1 H, CH_aH_b), 1.87 (ddd, *J* = 13.6, 4.4, 1.8, 1 H, CH_aH_b), 4.40 (s, 2 H, $=CH_2$), 4.64–4.65 (m, 1 H, CHOTMS), 4.93–4.98 (m, 1 H, $CHOSiEt_2$), 6.19 (dd, *J* = 15.8, 5.5, 1 H, =CHCHO), 6.62 (d, *J* = 15.8, 1 H, PhCH=), 7.19–7.38 (stack, 5 H, C_6H_5)	0.2, 5.4, 6.4, 6.5, 7.6, 43.8, 68.5, 68.9, 71.1, 91.8, 126.4, 127.2, 128.4, 128.7, 132.8, 137.1, 207.6	411 [100, (M + Na + MeOH)$^+$], 395 (45), 339 (15)	*m/z* [(M + Na)$^+$] calcd for $C_{21}H_{32}O_2Si_2$ + Na: 395.1839; found: 395.1845	73
d	0.01 [s, 9 H, $Si(CH_3)_3$], 0.64–0.79 [stack, 4 H, $Si(CH_2CH_3)_2$], 0.90–0.98 [stack, 6 H, $Si(CH_2CH_3)_2$], 1.04 {s, 21 H, $Si[CH(CH_3)_2]_3$}, 1.90–1.98 (stack, 2 H, CH_2), 4.45–4.58 (ABX, $J_{A,B}$ = 11.0, 2 H, $=CH_2$), 4.76–4.80 (m, 1 H, CHOTMS), 4.98 (dd, *J* = 4.8, 4.5, 1 H, $CHOSiEt_2$)	–0.1, 6.3, 6.4, 6.5, 7.0, 11.2, 18.6, 44.0, 61.6, 68.0, 71.0, 85.1, 94.1, 108.2, 206.8	473 (100)	*m/z* [(M + Na)$^+$] calcd for $C_{24}H_{46}O_2Si_3$ + Na: 473.2703; found: 473.2699	85
e	0.08 [s, 9 H, $Si(CH_3)_3$], 0.59–0.77 [stack, 4 H, $Si(CH_2CH_3)_2$], 0.95 [t, *J* = 8.7, 6 H, $Si(CH_2CH_3)_2$], 1.00–1.32 (stack, 6 H), 1.50–1.80 (stack, 7 H), 3.98–4.03 (m, 1 H, CHO), 4.35 (s, 2 H, $=CH_2$), 4.60–4.61 (m, 1 H, CHO)	0.2, 5.4, 6.4, 6.5, 7.4, 26.37, 26.43, 26.7, 28.1, 28.8, 39.9, 44.3, 68.4, 71.46, 71.49, 92.5, 207.5	375 (100)	*m/z* [(M + Na)$^+$] calcd for $C_{19}H_{36}O_2Si_2$ + Na: 375.2152; found: 375.2166	68
f	0.09 [s, 9 H, $Si(CH_3)_3$], 0.60–0.70 (stack, 2 H, CH_2CH_3), 0.71–0.80 (stack, 2 H, CH_2CH_3), 0.87–0.90 [stack, 6 H, $CH(CH_3)_2$], 0.92–0.99 [stack, 6 H, $Si(CH_2CH_3)_2$], 1.08–1.17 (m, 1 H), 1.39–1.50 (stack, 2 H), 1.65–1.73 (m, 1 H), 1.73–1.86 (m, 1 H), 4.26–4.33 (m, 1 H, $CHOSiEt_2$), 4.36 (s, 2 H, $=CH_2$), 4.57–4.58 (m, 1 H, CHOTMS)	0.2, 5.4, 6.4, 6.5, 7.1, 22.2, 23.2, 24.4, 43.8, 47.3, 65.8, 68.5, 71.3, 92.3, 207.6	349.2 (100)	*m/z* [(M + Na)$^+$] calcd for $C_{17}H_{34}O_2Si_2$ + Na: 349.1995; found: 349.2002	83
g	0.09 [s, 9 H, $Si(CH_3)_3$], 0.58–0.80 [stack, 4 H, $Si(CH_2CH_3)_2$], 0.86–0.98 [stack, 9 H, $Si(CH_2CH_3)_2$, CH_3], 1.24–1.44 (stack, 6 H), 1.46–1.53 (m, 1 H), 1.70 (ddd, *J* = 13.6, 4.4, 1.8, 1 H), 4.18–4.23 (m, 1 H, BuCHO), 4.36 (s, 2 H, $=CH_2$), 4.57–4.59 (m, 1 H, CHOTMS)	0.2, 5.4, 6.4, 6.5, 7.2, 14.2, 22.8, 27.6, 38.0, 43.2, 67.7, 68.5, 71.3, 92.3, 207.6	349.2 (100), 304.3 (7)	*m/z* [(M + Na)$^+$] calcd for $C_{17}H_{34}O_2Si_2$ + Na: 349.1995; found: 349.1992	66
h	0.09 [s, 9 H, $Si(CH_3)_3$], 0.57–0.69 (stack, 2 H, CH_2CH_3), 0.70–0.79 (stack, 2 H, CH_2CH_3), 0.91–0.99 [stack, 6 H, $Si(CH_2CH_3)_2$], 1.55–1.61 (m, 1 H), 1.70–1.77 (stack, 3 H), 3.59–3.63 (stack, 2 H, CH_2OBn), 4.36 (s, 2 H, $=CH_2$), 4.41–4.46 (m, 1 H, CHO), 4.50 (s, 2 H, $PhCH_2$), 4.58–4.59 (m, 1 H, CHO), 7.24–7.35 (stack, 5 H, C_6H_5)	0.1, 5.3, 6.3, 6.4, 7.2, 38.3, 43.5, 65.0, 67.1, 68.6, 71.2, 73.1, 92.1, 127.4, 127.5, 128.3, 138.7, 207.5	427.2 (100)	*m/z* [(M + Na)$^+$] calcd for $C_{22}H_{36}O_3Si_2$ + Na: 427.2101; found: 427.2105	70

Table 4 Characterisation Data for Allenes **5** (continued)

5[a]	^{1}H NMR ($CDCl_3$, 300 MHz) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$, 75 MHz), δ	TOF-MS *m/z* (%)	HRMS	Yield (%)
i	0.09 [s, 9 H, $Si(CH_3)_3$], 0.63–0.79 [stack, 4 H, $Si(CH_2CH_3)_2$], 0.93–0.99 [stack, 6 H, $Si(CH_2CH_3)_2$], 1.18 (d, *J* = 6.2, 3 H, CH_3), 1.48–1.56 (m, 1 H, CH_aH_b), 1.70 (ddd, *J* = 15.5, 4.6, 1.9, 1 H, CH_aH_b), 4.37 (s, 2 H, $=CH_2$), 4.40–4.46 (m, 1 H, CH_3CHO), 4.57 (dd, *J* = 4.4, 1.9, 1 H, CHOTMS)	0.1, 5.4, 6.3, 6.4, 7.4, 24.4, 45.1, 64.0, 68.6, 71.3, 91.8, 207.7	307.2 (100), 213.1 (45)	*m/z* [$(M + Na)^+$] calcd for $C_{14}H_{28}O_2Si_2$ + Na: 307.1526; found: 307.1534	67

[a] All compounds showed the characteristic peak for allenyl group. IR (film): 1936s cm^{-1} (C=C=C).

Formation of Acetonides 14 and 15

A mixture of the allene **5a** (100 mg, 0.27 mmol), KF (40 mg, 0.81 mmol) and $KHCO_3$ (80 mg, 0.81 mmol) in THF–MeOH (1:1, 1 mL) was heated at 70 °C for 1.5 h. After cooling, the mixture was diluted with H_2O (4 mL) and extracted with EtOAc (5 × 2 mL). The combined organic phases were washed with brine (4 mL) and then dried ($MgSO_4$). Concentration under reduced pressure followed by purification of the residue by flash column chromatography (eluent: 40% EtOAc in hexane) afforded a mixture of the diols **12** and **13** as a colourless oil (36 mg, 76%, **12**:**13**, ~1:3), which was used directly in the next step: Na_2SO_4 (48 mg, 0.34 mmol) and *p*-TsOH·H_2O (3 mg, 0.01 mmol) were added to a solution of diols **12** and **13** (36 mg, 0.19 mmol) in acetone (3 mL). The resulting mixture was stirred overnight and then poured into $NaHCO_3$ solution (3 mL). The phases were separated and the aqueous layer extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine (5 mL) and then dried ($MgSO_4$). Filtration and evaporation of the volatiles under reduced pressure provided a mixture of the acetonides **14** and **15** (44 mg, quant) as a colourless oil.

Selected Data for Alkyne **14**

^{13}C NMR (125 MHz, C_6D_6): δ = 3.7 ($C{\equiv}CCH_3$), 19.5 (CH_{3ax}), 30.3 (CH_{3eq}), 39.8 (CH_2), 60.8 ($CHC{\equiv}C$), 71.2 (PhCH), 77.8 ($C{\equiv}CCH_3$), 81.3 ($C{\equiv}CCH_3$), 99.7 [$C(CH_3)_2$], 126.0 (*o*-Ph), 127.8 (*p*-Ph), 128.5 (*m*-Ph), 141.6 (*ipso*-Ph).

Selected Data for Allene **15**

^{13}C NMR (125 MHz, C_6D_6): δ = 19.7 (CH_{3ax}), 30.3 (CH_{3eq}), 38.9 (CH_2), 67.8 (=CHCH), 71.4 (PhCH), 77.2 (CH_2=C=CH), 92.4 (CH_2=C=CH), 99.5 [$C(CH_3)_2$], 125.9 (*o*-Ph), 127.6 (*p*-Ph), 128.4 (*m*-Ph), 142.1 (*ipso*-Ph), 208.3 (CH_2=C=CH).

Acknowledgment

We thank Merck, Sharp & Dohme and the University of Birmingham for a studentship to R.R., and the Engineering and Physical Sciences Research Council (Grant No. GR/N32556) for a studentship to J.B.

References

(1) Current address: Metcalf Center for Science and Engineering, Boston University, 590, Commonwealth Avenue, Boston, MA 02215-2521, USA.
(2) For general reviews on the use of the 'Temporary Connection' in synthesis: (a) Cox, L. R.; Ley, S. V. In *Templated Organic Synthesis*; Diederich, F.; Stang, P. J., Eds.; Wiley-VCH: Weinheim, **2000**, Chap. 10, 275–375. (b) Bols, M.; Skrydstrup, T. *Chem. Rev.* **1995**, *95*, 1253. (c) Fensterbank, L.; Malacria, M.; Sieburth, S. M. *Synthesis* **1997**, 813. (d) Gauthier, D. R. Jr.; Zandi, K. S.; Shea, K. J. *Tetrahedron* **1998**, *54*, 2289.
(3) Beignet, J.; Cox, L. R. *Org. Lett.* **2003**, *5*, 4231.
(4) Tri-*tert*-butylpyrimidine (TTBP) and 2,6-di-*tert*-butyl-4-methylpyridine (2,6-DTBMP) were equally effective in this role.
(5) Evans, D. A.; Dart, M. J.; Duffy, J. L.; Yang, M. G. *J. Am. Chem. Soc.* **1996**, *118*, 4322.
(6) Beignet, J. *Ph.D. Thesis*; University of Birmingham: Birmingham, **2004**.
(7) Beignet, J.; Tiernan, J.; Woo, C. H.; Kariuki, B. M.; Cox, L. R. *J. Org. Chem.* **2004**, *69*, 6341.
(8) (a) Stragies, R.; Blechert, S. *Tetrahedron* **1999**, *55*, 8179. (b) Bradley, G. W.; Thomas, E. J. *Synlett* **1997**, 629. (c) Angoh, A. G.; Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1984**, 534.
(9) The *E*-stereochemical outcome of this side-reaction is in accord with mechanistic studies on this type of E′ elimination: (a) Matassa, V. G.; Jenkins, P. R.; Kümin, A.; Damm, L.; Schreiber, J.; Felix, D.; Zass, E.; Eschenmoser, A. *Isr. J. Chem.* **1989**, *29*, 321. (b) Fleming, I.; Morgan, I. T.; Sarkar, A. K. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2749.
(10) For some recent examples of allenylsilanes in synthesis: (a) Pacheco, M. C.; Gouverneur, V. *Org. Lett.* **2005**, *7*, 1267. (b) Daidouji, K.; Fuchibe, K.; Akiyama, T. *Org. Lett.* **2005**, *7*, 1051. (c) Archibald, S. C.; Barden, D. J.; Bazin, J. F. Y.; Fleming, I.; Foster, C. F.; Mandal, A. K.; Mandal, A. K.; Parker, D.; Takaki, K.; Ware, A. C.; Williams, A. R. B.; Zwicky, A. B. *Org. Biomol. Chem.* **2004**, *2*, 1051. (d) Buckle, M. J. C.; Fleming, I.; Gil, S.; Pang, K. L. C. *Org. Biomol. Chem.* **2004**, *2*, 749. (e) Denmark, S. E.; Gomez, L. *Heterocycles* **2002**, *58*, 129. (f) See also: Pornet, J. In *Science of Synthesis*; Fleming, I., Ed.; Georg Thieme Verlag: Stuttgart, **2002**, Chap. 4.4.32, 669–683; and references cited therein.
(11) The silyl tether is part of a vinylsilane in this intermediate and will be less effective in stabilising the β-vinyl carbocation on geometric grounds.
(12) For some recent examples of propargylsilanes in synthesis: (a) Patel, P. P.; Zhu, Y.; Zhang, L.; Herndon, J. W. *J. Organomet. Chem.* **2004**, *689*, 3379. (b) Nishikawa, T.; Mishima, Y.; Ohyabu, N.; Isobe, M. *Tetrahedron Lett.* **2004**, *45*, 175. (c) Niimi, L.; Shiino, K.; Hiraoka, S.; Yokozawa, T. *Macromolecules* **2002**, *35*, 3490. (d) Billet, M.; Schoenfelder, A.; Klotz, P.; Mann, A. *Tetrahedron Lett.* **2002**, *43*, 1453.
(13) For recent examples where propargylsilanes have been employed in intramolecular reactions: (a) Shin, C.; Chavre, S. N.; Pae, A. N.; Cha, J. H.; Koh, H. Y.; Chang, M. H.; Choi, J. H.; Cho, Y. S. *Org. Lett.* **2005**, *7*, 3283. (b) Dziedzic, M.; Lipner, G.; Furman, B. *Tetrahedron Lett.* **2005**, *46*, 6861. (c) Dziedzic, M.; Lipner, G.; Illangua, J. M.; Furman, B. *Tetrahedron* **2005**, *61*, 8641; and references cited therein.

(14) (a) Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8678. (b) Pornet, J.; Kolani, N.; Mesnard, D.; Miginiac, L.; Jaworski, K. *J. Organomet. Chem.* **1982**, *236*, 177. (c) Marshall, J. A.; Robinson, E. D.; Lebreton, J. *J. Org. Chem.* **1990**, *55*, 227.
(15) Propargyltrimethylsilane is commercially available although expensive and invariably contaminated with varying amounts of allenyltrimethylsilane. We find it more convenient to prepare the reagent ourselves.
(16) Tamao, K.; Nakajo, E.; Ito, Y. *Tetrahedron* **1988**, *44*, 3997.
(17) The β-hydroxy esters were prepared uneventfully by a Reformatski reaction between ethyl bromoacetate and the corresponding aldehyde: Picotin, G.; Miginiac, P. *J. Org. Chem.* **1987**, *52*, 4796.
(18) Crich, D.; Smith, M.; Yao, Q.; Picione, J. *Synthesis* **2001**, 323.
(19) Ley, S. V.; Baxendale, I. R.; Bream, R. N.; Jackson, P. S.; Leach, A. G.; Longbottom, D. A.; Nesi, M.; Scott, J. S.; Storer, R. I.; Taylor, S. J. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3815; and references cited therein.
(20) 2,6-Di-*tert*-butylpyridine bound through the 4-position to a polystyrene support (1% divinylbenzene) is available from Aldrich or Fluka: Wright, M. E.; Pulley, S. R. *J. Org. Chem.* **1987**, *52*, 1623.
(21) Allylsilanes are particularly susceptible to decomposition in the presence of Brønsted acids: Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761; and references cited therein.
(22) Oda, H.; Sato, M.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron* **1984**, *41*, 3257.
(23) Rychnovsky, S. D.; Rogers, B.; Yang, G. *J. Org. Chem.* **1993**, *58*, 3511.